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ALKALOIDS OF *URGINEA ALTISSIMA* AND THEIR ANTIMICROBIAL ACTIVITY AGAINST *PHYTOPHTHORA CAPSICI*

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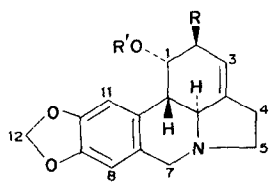
Key Word Index—*Urginea altissima*, Liliaceae, alkaloids, lycorine, acetylcaranine, antimicrobial activity; *Phytophthora capsici*

Plant and source. Urginea altissima Bak. Plant material was collected at northern part of the Lake Rudolf, Ethiopia.

Present work. 950g of fresh bulb tissues were extracted with MeOH. The extract showed considerable antimicrobial activity against *Phytophthora capsici*. This activity was located in the water-soluble part of the extract which (chromatographed over alumina) gave lycorine [1], (**1**), mp 273–278°, $[\alpha]_D^{22°}$ −125·3° (EtOH), (IR, NMR) as an active component. Lycorine showed protective activity against blight (*P. capsici*) of tomato plants, when an aq. soln (500 μg/ml) was sprayed on the leaves. The HCl salt exhibited a slight enhancement in activity, but diacetyllycorine, dihydrolycorine and 2-acetyllycorine possessed lower activity than that of lycorine itself.

The $CHCl_3$ soluble part of MeOH extract (chromatographed over Si gel, TLC) gave the alkaloid, acetylcaranine (**2**), $C_{18}H_{19}NO_4$, M^+ 313, mp 173–174°, $[\alpha]_D^{22°}$ −80·5° ($CHCl_3$), ν_{max} 1735 cm^{-1} (acetate), λ_{max}^{MeOH} 290nm (ε, 2900), NMR ($CDCl_3$, TMS): δ 6·72, 6·57 (each 1H, *s*, for H-11, H-8), 5·89 (2H, *s*, for H-12 methylene dioxy), 5·85† (1H, *br s*, for H-1), 5·40 (1H, *br s*, for H-3), 4·15, 3·53 (each 1H, *d*, *J* 15 Hz, for H-7α, H-7β and 1·91 (3H, *s*, for acetyl–Me). (**2**) was identical with an authentic specimen (derived from caranine by acetylation; mmp, IR, NMR). This is the first report of (**2**) as a natural product.



(**1**) Lycorine R = OH R′ = H
(**2**) Acetylcaranine R = H R′ = Ac

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† The extraordinary low field shift of H-1 appears to be benzene ring anisotropy and van der Waals' effect between H-1, H-11 protons, the latter was evident on a NOE experiment

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TETRANORTRITERPENOIDS FROM THE HEARTWOOD OF *CARAPA GUIANENSIS*

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Key Word Index—*Carapa guianensis*, Meliaceae, 6α11β-diacetoxygedunin; 6α-acetoxygedunin

Plant. Carapa guianensis Aubl. (Meliaceae). *Previous work.* The seeds of this plant have yielded several tetranortriterpenoids [1,2]. The heartwood, obtained from Trinidad, West Indies, has

shown 11β-acetoxygedunin and 6α,11β-diacetoxygedunin [3]

Present work. We re-investigated the heartwood of this plant, obtained locally, and were able to isolate 6α,11β-diacetoxygedunin (**1**) and 6α-acetoxygedunin (**2**). The latter has not been previously reported from the heartwood.

The $CHCl_3$-soluble fraction of the EtAc extract of the ground heartwood yielded by PLC two crystalline compounds. 6α,11β-diacetoxygedunin (**1**) and 6α-acetoxygedunin (**2**).

6α,11β-diacetoxygedunin (**1**) crystallized from MeOH mp 195–196°, 247–248°; λ_{max} 222 nm (ε 11500); ν_{max} 1740–1750, 1675 and 874 cm^{-1}. On mild alkaline hydrolysis the compound yielded the expected triol 6α,7α,11β-trihydroxy-7-deacetoxygedunin (**3**) which crystallized from EtOAc mp 266–268°; λ_{max} 218 nm (ε 10700); IR ν_{max} 3470, 1740, 1650 and 870 cm^{-1}. Acetylation of the above triol (**3**) with Ac_2O–pyridine at room temp. gave the diacetate 7-hydroxy-6α,11β-diacetoxy-7-deacetoxygedunin (**4**) as crystals from EtOAc mp 289–291°, λ_{max} 218 nm (ε 10600); ν_{max} 3470, 1735, 1675 and 874 cm^{-1}.

A comparison of the NMR spectrum of this diacetate (**4**) with that of the naturally occurring triacetate 6α,11β-diacetoxygedunin (**1**) confirmed that it was the product which under these conditions resulted from the C_7 hydroxyl resisting acetylation. Thus, there were 2 acetoxy methyl signals in the NMR (δ 2.12, 2.19). In addition there were 2 protons (C<u>H</u>OAc) centred at δ 5.76 and δ5·34 which corresponded in both shape and position to those assigned to the C_{11} and C_6 protons respectively of the naturally occurring triacetate [3]. A broad signal in the spectrum of the diacetate (**4**) at δ 3.51 replaced the doublet at δ 4·89 which had been assigned to the C_7 proton of 6α,11β-diacetoxygedunin. On shaking with D_2O the signal sharpened to a doublet (*J* 3 Hz) and must be the proton on the hydroxyl bearing C_7.

6α-Acetoxygedunin (**2**) crystallized from EtOAc–light petroleum mp 270–273°; λ_{max} 220 nm (ε 10000); ν_{max} 1760, 1740, 1670 and 870 cm^{-1}. The signals in the NMR spectrum corresponded to those reported previously [2].

EXPERIMENTAL

IR spectra were in Nujol and UV in EtOH. TLC and PLC were on Si gel (Merck 60 $PF_{254+366}$). Mp's are uncorrected. Light petrol was bp 60–80°.

Extraction and isolation. Ground heartwood (4 kg) was extracted with EtOAc (19 l) for 2 days. The reddish-brown extract was evaporated to dryness and the $CHCl_3$-soluble residue (17 g) washed with light petrol leaving an insoluble gum (13·6 g). PLC (1·8 g) on a large plate (40 × 60 cm, 2 mm thick) with light petrol–acetone (3:1) gave 2 main bands. The band of higher R_f gave, on repeated PLC, crystalline 6α-acetoxygedunin (333 mg) and that of lower R_f gave 6α,11β-diacetoxygedunin (157 mg).

6α,11β-Diacetoxygedunin (**1**): mp 195–196°, 247–248°, M^+ 598 (Found: C, 63·9; H, 6·5. Calc. for $C_{32}H_{38}O_{12}$: C, 64·2; H, 6·4%).

6α,7α,11β-Trihydroxy-7-deacetoxygedunin (**3**). Treatment of 6α,11β-diacetoxygedunin (100 mg) with 5% KOH–MeOH (5 ml) overnight at R.T. gave the triol (60 mg) mp 266–268°, M^+ 472 (Found: C, 65·9; H, 7·0. $C_{26}H_{32}O_8$ requires: C, 66·1; H, 6·8%).

7α-Hydroxy-6α,11β-diacetoxy-7-deacetoxygedunin (**4**) was obtained by dissolving the triol (**3**) in Ac_2O (2 ml) and pyridine (2 ml) and standing at room temp. overnight. Work up in the usual way gave the diacetate (95 mg) mp 289–291°, M^+ 556 (Found: C, 64·0; H, 6·5. $C_{30}H_{36}O_{10}$ requires: C, 64·7; H, 6·5%). NMR (100 MHz, $CDCl_3$): δ 1·22 (3H, *s*), 1·30 (3H, *s*), 1·34 (3H, *s*), 1·43 (6H, *s*), 2·12 (3H, *s*), 2·19 (3H, *s*), 2·68 (1H, *d*, *J* 5 Hz), 2·73 (1H, *d*, *J* 12 Hz), 3·51 (1H, *m*, $W_{1/2}$ 6 Hz), 3·83 (1H, *s*), 5·34 (1H, *q*, *J* 3, 12 Hz), 5·59 (1H, *s*), 5·76 (1H, *m*, $W_{1/2}$ 21 Hz), 5·92 (1H, *d*, *J* 10 Hz), 6·30 (1H, *m*), 7·11 (1H, *d*, *J* 10 Hz), 7·38 (2H, *m*).

6α-Acetoxygedunin (**2**): Mp 270–273°, M^+ 540 (Found: C, 66·3; H, 6·8. Calc. for $C_{30}H_{36}O_9$: C, 66·6; H, 6·7%). NMR (60 MHz, $CDCl_3$): δ 1·18 (3H, *s*), 1·22 (3H, *s*), 1·29 (9H, *s*), 2·04 (3H, *s*), 2·16 (3H, *s*), 2·55 (1H, *d*, *J* 13 Hz), 3·65 (1H, *s*), 4·94 (1H, *d*, *J* 3 Hz), 5·34 (1H, *q*, *J* 3, 13 Hz), 5·66 (1H, *s*), 5·99 (1H, *d*, *J* 10 Hz), 6·41 (1H, *m*), 7·16 (1H, *d*, *J* 10 Hz), 7·50 (2H, *m*).

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